(19)Japanese Patent Office (JP)

(12) LAID-OPEN PATENT PUBLICATION (A)

(11) Laid-Open Number OF Patent Application

Tokkai Hei.8-97161

(43) Laid-Open Date: April 12, 1996

(51) Int Cl.[6]	Identification Mark	Office Reference Number	F1
H01L 21/205			
C23C 16/50			
G03G 5/08	360		

Request For Examination: not requested

Number of Claims: 22 FD (20 pages in total)

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(54)Title of The Invention: Deposited film-forming method and deposited film-forming apparatus by a high frequency plasma CVD process

(57) Abstract:

[Object] The present invention provides a method for forming a deposited film having excellent properties and a deposited film-forming apparatus. Particularly, the present invention provides a deposited film-forming method and a deposited film-forming apparatus which enable one to efficiently prepare an electrophotographic light receiving member or the like having a high quality and a high performance at a good yield.

[Constitution] A deposited film-forming method by a high frequency plasma CVD process by introducing a raw material gas, a first electromagnetic wave having a first frequency and a second electromagnetic wave having a second frequency which is different from said first frequency into a discharge space of a reaction vessel formed to have an air-tight structure to generate glow discharge whereby forming a deposited film on a substrate arranged in said glow discharge space, characterized in that each of said first and second electromagnetic waves is made to have a prescribed frequency, and after elapse of a prescribed time since the introduction of said first electromagnetic wave, said second electromagnetic wave is introduced, wherein stability and uniformity of a plasma generated at an initial stage of said glow discharge are achieved singly by said first electromagnetic wave, and a deposited-film forming speed is optimized by overlapping said second electromagnetic wave, whereby a deposited film having excellent properties is formed on said substrate.

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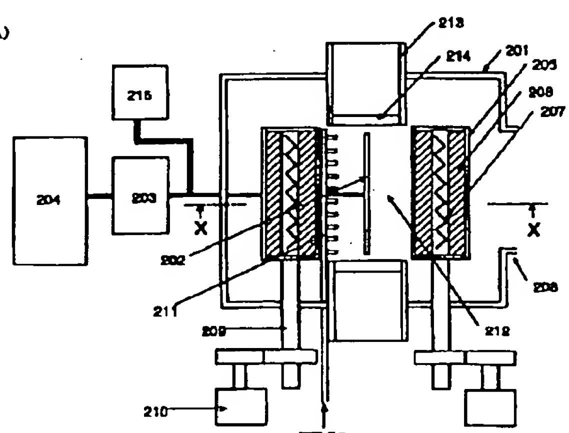

【Claims】

【Claim 1】 A deposited film-forming method by a high frequency plasma CVD process by introducing a raw material gas, a first electromagnetic wave having a first frequency and a second electromagnetic wave having a second frequency which is different from said first frequency into a discharge space of a reaction vessel formed to have an air-tight structure to generate glow discharge whereby forming a deposited film on a substrate arranged in said glow discharge space, characterized in that each of said first and second electromagnetic waves is made to have a prescribed frequency, and after elapse of a prescribed time since the introduction of said first electromagnetic wave, said second electromagnetic wave is introduced, wherein stability and uniformity of a plasma generated at an initial stage of said glow discharge are achieved singly by said first electromagnetic wave, and a deposited-film forming speed is optimized by overlapping said second electromagnetic wave, whereby a deposited film having excellent properties is formed on said substrate.

【Claim 2】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 1, characterized in that the electromagnetic wave having a second frequency is introduced within a period of 1 to 10 minutes after the electromagnetic wave having a first frequency is introduced.

【Claim 3】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 1, characterized in that the electromagnetic wave having a second frequency is introduced within a period of 0.05 second to 5 minutes after the electromagnetic wave having a first frequency is introduced and

discharge is generated.

【Claim 4】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 1, characterized in that the electromagnetic wave having a second frequency is introduced within a period of 0.05 second to 3 minutes after the electromagnetic wave having a first frequency is introduced, discharge is generated and said discharge is stabilized.

【Claim 5】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 4, characterized in that the stability of said discharge by the electromagnetic wave having a first frequency is determined by a change rate of an inner pressure and/or that of a luminance of the discharge during the discharging.

【Claim 6】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 5, characterized in that the change rate of the inner pressure and/or the change rate of the luminance are within a range of 5%.

【Claim 7】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 1, characterized in that the two different electromagnetic waves each having a different frequency are separately introduced into the reaction vessel respectively through a different introduction means.

【Claim 8】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 7, characterized in that at least one of the different introduction means comprises a waveguide and the other comprises a cathode electrode.

【Claim 9】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 1, characterized in that at

least one of the two different electromagnetic waves each having a different frequency which are introduced into the reaction vessel comprises a microwave and the other comprises a high frequency.

【Claim 10】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 9, characterized in that the microwave includes at least a microwave with a frequency of 2.45 GHz.

【Claim 11】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 9 or 10, characterized in that the high frequency includes at least a high frequency with a frequency in a range of 20 MHz to 450 MHz.

【Claim 12】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 9, characterized in that the microwave is introduced into the discharge space of the reaction vessel through a waveguide and the high frequency is introduced through a cathode electrode provided in the discharge space.

【Claim 13】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 9, characterized in that the microwave is introduced into the discharge space of the reaction vessel through a waveguide from upper and lower directions of the discharge space and the high frequency is introduced from a direction where a high frequency introduction electrode is deviated by 10° or more with respect to a direction of a strong electric field generated by the microwave.

【Claim 14】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 9, characterized in that when each of the microwave and the high frequency is singly

introduced, an energy of each of the microwave and the high frequency is less than 150% of the energy thereof when a film deposition rate is saturated, and a ratio of the microwave energy/the high frequency energy is in a range of 0.05 to 2.0.

【Claim 15】 The deposited film-forming method by a high frequency plasma CVD process defined in any of claims 1 to 13, characterized in that a direct current bias is additionally applied in addition to the high frequency.

【Claim 16】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 14, characterized in that the stability of the discharge by the electromagnetic wave having a first frequency is specified by a change rate of a current flown when the bias voltage is applied.

【Claim 17】 The deposited film-forming method by a high frequency plasma CVD process defined in claim 15, characterized in that the change rate of the current flown when the bias voltage is applied is made to be within 5%.

【Claim 18】 The deposited film-forming method by a high frequency plasma CVD process defined in any of claims 1 to 16, characterized in that a rotary cylindrical substrate as the substrate is rotated at a rotating speed where the thickness of a deposited film formed on said substrate at one revolution is less than 2000 Å to form a deposited film on the substrate.

【Claim 19】 A deposited film-forming apparatus comprising a reaction vessel having a discharge space in which a substrate is capable of being arranged, a raw material gas introduction means and an electromagnetic wave introduction means, wherein said electromagnetic wave introduction means has at least a first

introduction means for introducing a first electromagnetic wave having a first frequency and a second introduction means for introducing a second electromagnetic wave having a second frequency which is different from said first frequency.

【Claim 20】 The deposited film-forming apparatus defined in claim 19, characterized in that the first introduction means comprises a waveguide.

【Claim 21】 The deposited film-forming apparatus defined in claim 19 or 20, characterized in that the second introduction means comprises a cathode electrode provided in the reaction vessel.

【Claim 22】 The deposited film-forming apparatus defined in any of claims 19 to 21, characterized in that a means for measuring an inner pressure and a means for measuring a luminance are provided in the reaction vessel.

【Detailed Description of the Invention】

【0001】

【Industrial field in which the invention is utilized】

The present invention relates to a deposited film-forming method and a deposited film-forming apparatus by a high frequency plasma CVD process which enable one to form, on a substrate, a deposited film, particularly a functional film, especially an amorphous semiconductor film which is used in a semiconductor device, an electrophotographic photosensitive device, an image input line sensor, an image pickup device or a photovoltaic device.

【0002】

【Prior Art】

As element members which are used in semiconductor devices, electrophotographic photosensitive devices, image input

line sensors, image pickup devices, photovoltaic devices, other various electronics elements, and optical elements, there have been proposed semiconductor deposited films comprising amorphous silicon materials such as amorphous silicon materials compensated, for instance, by hydrogen and/or halogen (for example, fluorine, chlorine, or the like)[hereinafter referred to as "a-Si:(H,X)]. And some of these deposited films have been using in practice. For the formation of these deposited films, there is known a film-forming method by means of a plasma CVD process, wherein a raw material gas is decomposed by way of glow discharge by means of a direct current, a high frequency or a microwave to form a deposited film in a foil state on a substrate comprising a glass, quartz, heat-resistant synthetic resin film, stainless steel, or aluminum. Various apparatus for practicing the film-forming method have been proposed.

[0003]

For example, Japanese Unexamined Patent Publication Sho.54-86341 discloses a technique concerning a light receiving member for use in electrophotography having a photoconductive layer comprising a-Si formed by means of RF plasma CVD and which excels in moisture resistance, durability, and electrical characteristics. Japanese Unexamined Patent Publication Sho.60-186849 discloses a deposited film-forming method by means of microwave plasma CVD with a frequency of 2.45 GHz as a decomposition source of a raw material gas. This deposited film-forming method is that the raw material gas utilization efficiency is markedly improved by arranging a plurality of substrates so as to circumscribe a microwave energy introduction portion to form an inner chamber (that is, a discharge space). Besides, as a means in order to form a deposited film having good

characteristics, there has been proposed a deposited film-forming technique using electromagnetic waves having a different frequency. For example, Japanese Unexamined Patent Publication Sho.56-45760 discloses a technique which makes it possible to stably form a deposited film having good characteristics on a substrate at a high deposition rate by exciting a reaction gas using a plurality of power sources with a different frequency as an excitation power source for exciting said reaction gas. And Japanese Unexamined Patent Publication Hei.2-213473 discloses a deposited film-forming method such that a plurality of substrates are arranged so as to circumscribe a microwave energy introduction portion to form an inner chamber (that is, a discharge space) and a discharge plasma is formed in the inner chamber by virtue of the microwave introduced therein to form a deposited film on each of the substrates, wherein by controlling the plasma potential by applying an alternate current voltage of 500 Hz to 2 MHz between the substrates upon forming the deposited film, it is possible to form electrophotographic light receiving members which slightly provide image defects and have good characteristics. By using electromagnetic waves having a different frequency in this way, it is possible to positively control the plasma stability, film deposition rate, and plasma potential. This situation makes it possible to obtain electrophotographic light receiving members, which are satisfactory in terms of the electrical characteristics at a certain level, at a yield which is satisfactory at a certain level.

【0004】

【Subjects that the invention is intended to solve】

However, in recent years, there is an increased demand for improving an electrophotographic image such that it has a higher image quality and is more finely resolved. In order to comply with this demand, there is a demand for developing a technique which enables one to stably produce a high quality electrophotographic light receiving member having a high performance at a high yield. The conventional technique is difficult to sufficiently cope with these demands. For instance, in the case of mass-producing an electrophotographic light receiving member by the foregoing conventional plasma CVD process using electromagnetic waves having a different frequency, although such advantages as previously described are provided, problems are liable to entail such that a variation is occurred among lots in terms of the characteristics and a variation in terms of the characteristics is occurred not only for the light receiving members obtained in the same lot but also for one of the light receiving member. In the past, the demand of image quality and fine resolution for an electrophotographic image was not so severe. Therefore, even when a variation in terms of the characteristics at a certain extent were present, there could be attained a yield of satisfactory level because there was a tolerance to a certain extent for the specification with respect to the characteristics required.

[0005]

However, along with the demand for improving an electrophotographic image such that it has a higher image quality and is more finely resolved has been increased in recent years as above described, the tolerance for the specification has been narrowed than that in the past. Particularly, in recent years, there

has been increased an occasion of reproducing a copy from an halftone original such as a photograph which is different from an original comprising mainly character images for which a copy has been reproduced in the past, and delicate unevenness in a reproduced image has become capable of optically recognized in many cases. As a result, a copy product which could be considered to be acceptable in the past has not considered to acceptable in recent years. This situation has resulted in a reduction in the yield. Therefore, also in an industrial viewpoint, it is an urgent necessity to develop a deposited film-forming method and a deposited film-forming apparatus which enable one to quantitatively produce an electrophotographic light receiving member, which can solve the foregoing problems, at a high yield.

【0006】

Consequently, the present invention is aimed at solving the foregoing problems found on the conventional deposited film-forming method and apparatus used for preparing an electrophotographic light receiving member having a light receiving layer comprising a-Si:(H, X). Particularly, an object of the present invention is to provide a deposited film-forming method and a deposited film-forming apparatus which enable one to form a deposited film which stably exhibits electric, optical and photoconductive characteristics without depending on use environments and which excels in durability. That is, the present invention provides a deposited film-forming method and a deposited film-forming apparatus which enable one to efficiently produce, for instance, a high quality and high performance electrophotographic light receiving member comprising a

non-single crystal material containing silicon atoms as a matrix.

【0007】

【Means to solve the subjects】

The present invention attains the above object and provides a deposited film-forming method by a high frequency plasma CVD process by introducing a raw material gas and at least a first electromagnetic wave having a first frequency and a second electromagnetic wave having a second frequency which is different from said first frequency into a discharge space of a reaction vessel formed to have an air-tight structure to generate glow discharge whereby forming a deposited film on a substrate arranged in said glow discharge space, characterized in that each of said first and second electromagnetic waves is made to have a prescribed frequency, and after elapse of a prescribed time since the introduction of said first electromagnetic wave, said second electromagnetic wave is introduced.

【0008】

For the introduction time of the electromagnetic waves, the electromagnetic wave having a second frequency is introduced preferably within a period of 1 to 10 minutes after the electromagnetic wave having a first frequency is introduced, more preferably within a period of 0.05 second to 5 minutes after the electromagnetic wave having a first frequency is introduced and discharge is generated, most preferably within a period of 0.05 second to 3 minutes after the electromagnetic wave having a first frequency is introduced, discharge is generated and said discharge is stabilized. For the stability of the discharge by the electromagnetic wave having a first frequency, it is determined

by a change rate of an inner pressure and/or that of a luminance of the discharge during the discharging. It is preferred that the change rate of the inner pressure and/or the change rate of the luminance are within a range of 5%. The two different electromagnetic waves each having a different frequency which are introduced into the reaction vessel include preferably a microwave having a frequency of 2.45 GHz and a high frequency having a frequency of 20 MHz to 450 MHz, more preferably a microwave having a frequency of 2.45 GHz and a high frequency having a frequency of 51 MHz to 250 MHz. It is preferred that these energies are separately introduced into the reaction vessel respectively through a different introduction means. Particularly, for instance, it is preferred to make such that the microwave energy is introduced into the discharge space of the reaction vessel through a waveguide and the high frequency energy is introduced through a cathode electrode provided in the discharge space. Specifically, it is preferred that the microwave energy is introduced into the discharge space of the reaction vessel through the waveguide from upper and lower directions of the discharge space and the high frequency energy is introduced from a direction where the high frequency introduction electrode is deviated by 10° or more with respect to a direction of a strong electric field generated by the microwave. When each of the microwave energy and the high frequency energy is singly introduced, it is preferred that each energy is less than 150% of the energy thereof when a film deposition rate is saturated, and a ratio of the microwave energy/the high frequency energy is in a range of 0.05 to 2.0. In the present invention, it is possible that

a direct current bias is additionally applied in addition to the high frequency. the stability of the discharge by the electromagnetic wave having a first frequency can be determined by monitoring a change rate of a current flown, for instance, when a bias voltage is applied. In this case, it is preferred for the change rate of the current flown to be within 5%. When a rotary cylindrical substrate is used as the substrate, it is preferred that the substrate is rotated at a rotating speed where the thickness of a deposited film formed on said substrate at one revolution is less than 2000 Å to form a deposited film on the substrate.

[0009]

The apparatus of the present invention comprises a reaction vessel having a discharge space in which a substrate is capable of being arranged, a raw material gas introduction means and an electromagnetic wave introduction means, wherein said electromagnetic wave introduction means has at least a first introduction means for introducing a first electromagnetic wave having a first frequency and a second introduction means for introducing a second electromagnetic wave having a second frequency which is different from said first frequency. If necessary, it is possible that a means for measuring an inner pressure and a means for measuring a luminance are provided in the reaction vessel.

[0010]

In the following, the deposited film-forming method and the deposited film-forming by means of high frequency plasma CVD according to the present invention will be described in more detail with reference to the drawings. FIG. 2 is a schematic explanatory

view of an example of a deposited film-forming apparatus by means of high frequency plasma CVD suitable for preparing an electrophotographic light receiving member in the present invention. FIG. 2A is a schematic longitudinal section view, and FIG. 2B is a schematic cross-sectional view taken along the line X-X in FIG. 2A. In the figures, reference numeral 201 indicates a reaction vessel formed to have air-tight structure. Reference numeral 202 indicates a cathode electrode which is electrically connected to a high frequency power source 204 capable of emitting an electromagnetic wave having a prescribed frequency of the present invention through a matching box 203. Reference numeral 215 indicates a direct current power source (a bias power source) for applying a direct current voltage to a bias electrode. The direct current power source is electrically connected to the cathode electrode as well as the high frequency power source. Reference numeral 214 indicates a microwave introduction dielectric window comprising a material (for example, quartz glass, alumina ceramics, or the like) which is capable of efficiently transmitting a microwave power into the reaction vessel 201 and is capable to hermetically seal the inside of the reaction vessel. Reference numeral 213 indicates a waveguide for transmitting a microwave power. The waveguide comprises a rectangular portion extending from the microwave power source to the vicinity of the reaction vessel and a cylindrical portion which is inserted in the reaction vessel. The waveguide 213 is electrically connected to the microwave power source (not shown) together with a stub tuner (not shown) and an isolator (not shown). The dielectric window 214 is hermetically fixed to the inner wall of the cylindrical portion of the waveguide

213 so as to maintain the inside atmosphere of the reaction vessel in an enclosed state. Reference numeral 208 indicates an exhaust pipe which is open in the reaction vessel 201 through one end portion thereof and is communicated with an exhaustion device (not shown) through the other end portion thereof. As the exhaust pipe and the exhaustion device, it is preferred to use ones for evacuating air in the reaction vessel and ones for exhausting film-forming gas (which is reacted or not reacted) in order to prevent residual gas in the exhaust pipe and the exhaustion device from being reacted with the air. In the reaction vessel 201, there are provided substrates 205, substrate holders 206, heaters 207 for heating the substrates, and a raw material gas introduction pipe 211. Reference numeral 209 indicates a rotary shaft capable of being rotated by a motor 210. Reference numeral 212 indicates a discharge space which is circumscribed by the substrates 205.

[0011]

The production of an electrophotographic photosensitive member using such apparatus as above described is conducted as follows. First, the inside of the reaction vessel 201 is evacuated through the exhaust pipe 208 by means of the exhaustion device (not shown) until the inner pressure of the reaction vessel 201 becomes to be less than 1×10^{-5} Torr. At this time, it is preferred that the evacuation at an initial stage is slowly conducted (that is, slow evacuation) in order to prevent dust and the like present in the reaction vessel from being blown up. Then, the substrates 205 are heated to and maintained at a prescribed temperature by means of the heaters 207. At this time, in order to improve the thermal conduction between the heaters and the substrates whereby uniformly heating the

substrates, it is possible that gas (for example, inert gas, hydrogen gas, or the like) which is stable to heat and is not reactive with the substrates is introduced into the reaction vessel. Separately, in the case where an oxide film is formed on the surface of the substrate, it is effective that the substrate-heating is conducted in an atmosphere containing oxygen. The substrate-heating means may comprise a heat-generating body of the vacuum specification. As specific examples, there can be mentioned electric resistance heat-generating bodies such as a heater comprising a sheath-like heater wound, a plate heater, and a ceramic heater, heat radiation lump heat-generating bodies such as a halogen lump, and an infrared lump, and heat-generating bodies comprising heat exchange means using a thermal medium comprising liquid or air. The surface of the heating means may be constituted by a metallic material such as stainless steel, nickel, aluminum, or copper, ceramics, or heat-resistant polymer resins. Besides, it is possible to adopt a manner wherein a heating vessel is provided in the reaction vessel, after heated, the substrates are transported into the reaction vessel in a vacuumed atmosphere.

【0012】

When the substrates are maintained at a prescribed temperature, the inside of the reaction vessel is once vacuumed, a raw material gas for forming a first layer is introduced into the reaction vessel through the cathode electrode 202 which also serves as the gas introduction pipe. Specifically, as the raw material gas for nC-Si:(H, X), for example, silane gas, diboran gas as a doping gas, and helium gas as a dilution gas are introduced into the reaction vessel. Concurrently with this, an electromagnetic wave having a frequency

of 20 to 450 MHz is generated by the high frequency power source 204, followed by being introduced into the reaction vessel 201 through the matching box 203 and the cathode electrode 202. After a prescribed period of time is elapsed, a microwave preferably having a frequency of 2.45 GHz is generated by the microwave power source (not shown), followed by being introduced into the reaction vessel 201 through the waveguide 213 and the dielectric window 214. Here, there is no particular limitation for the introduction order of the high frequency energy and the microwave energy, and it is possible that any of them is firstly introduced. For the electromagnetic waves introduced and their frequencies, a combination of a microwave having a frequency of 2.45 GHz and a high frequency having a frequency of 20 MHz to 450 MHz is preferable, and a combination of said microwave and a high frequency having a frequency of 51 MHz to 250 MHz is more preferable in the present invention. There is no particular limitation for the introduction manner for the microwave power and the high frequency power. However, the microwave power and the high frequency power are preferred to be separately introduced respectively through an independent introduction means in order to control each power as desired. Particularly, by introducing the microwave energy into the discharge space through the waveguide and introducing the high frequency energy through the cathode electrode provided in the discharge space, the stability and the uniformity of the plasma can be more improved. This situation has been confirmed through experiments. In this case, it is preferred that the high frequency energy is introduced into the discharge space from a direction where the cathode electrode is deviated by 10° or more with respect to a direction of a strong electric field

generated by the microwave. In this case, the plasma is prevented from being disturbed by the cathode electrode. There is no particular limitation for the introduction order for the microwave and the high frequency as previously described. However, since the high frequency has a wider range for the conditions (the inner pressure, the substrate temperature, the gas flow rate, and the like) to cause discharge in comparison with the microwave, it is preferred to firstly introduce the high frequency, where even when the discharging conditions are changed, the plasma is readily stabilized. With respect to the power condition, when each of the microwave energy and the high frequency energy is singly introduced, it is preferred that each energy is less than 150% of the energy thereof when a film deposition rate is saturated, and a ratio of the microwave energy/the high frequency energy is in a range of 0.05 to 2.0. For the ratio of the microwave energy/the high frequency energy to be in a range of 0.05 to 2.0, when the proportion of the microwave power is made to be greater than said ratio, the effect of overlapping the high frequency is diminished. This is because the effect of improving the deposition rate of a deposited film by overlapping two kinds of high frequencies while attaining an effect of improving the characteristics of the deposited film is diminished. With respect to the respective single power, when the deposition rate of the deposited film by a single energy of the microwave or the high frequency is more than 150% of the energy with which said deposition rate is saturated, the effect by overlapping the two kinds of frequencies is diminished. For the reason for this, it is considered such that the state of the plasma is governed by the energy of more than 150%. Similarly, when a

combination of the both energies exceeds 150% of the single energy with which the deposition rate of the deposited film is saturated, it is difficult to control the plasma as desired because of excessive energy.

[0013]

In the present invention, because the energy of the electromagnetic wave is introduced through the cathode, by optimizing the number of the cathode, the form thereof and the size thereof, the uniformity of the plasma can be more improved. In the present invention, in order to uniform the plasma, it is possible to use a plurality of cathodes. However, when the number of the cathode electrodes is excessive, there is entailed a problem in that the discharge is disturbed. Therefore, the number of the cathode electrodes is preferably 20 or less, more preferably 15 or less, most preferably 10 or less. The form (the cross section form) of the cathode electrode may be polygonal or round. However, in order to uniformly introduce the electromagnetic wave, the cathode electrode is preferred to be shaped in a symmetrical form such as a round form or a regular polygonal form. The cross section area of the cathode electrode is preferably in a range of 1 mm^2 to 800 cm^2, more preferably in a range of 3 mm^2 to 500 cm^2, most preferably in a range of 5 mm^2 to 350 cm^2. Separately, when the cathode electrode comprises a cylindrical cathode electrode, the diameter of the cross section thereof is preferably in a range of 1 mm to 15 cm, more preferably in a range of 2 mm to 12 cm, most preferably in a range of 3 mm to 10 cm. For the length of the cathode electrode, although being different depending on the length of the substrate, it is preferably of 5% to 200% of the length of the substrate, more preferably of

10% to 180%, most preferably of 20% to 150%. There is no particular limitation for the constituent material of the cathode electrode as long as it is capable of transmitting an electromagnetic wave. As such material, there can be mentioned, for example, metals such as Al, Cr, Mo, Au, In, Nb, Te, V, Ti, Pt, Pb, and Fe, and alloys of these metals such as stainless steels (for example, SUS 300 series and SUS 400 series under JIS Standard).

【0014】

If necessary, a direct current voltage is applied between the bias electrode 202 in the discharge space 212 and the substrates 205. In this way, in the discharge space 212 circumscribed by the substrates 205, the raw material gas is excited and dissociated by the energy of the high frequency of 20 to 450 MHz and the energy of the microwave energy to produce active species including neutral radical particles, ion particles and electrons, where these active species are mutually reacted to cause the formation of a deposited film on the surface of each of the substrates 205. In this case, when the bias voltage is applied as above described, the ions in the discharge space are accelerated to collide with the surface of each of the substrates to thereby imparting surface mobility to the active species on the substrates, whereby the deposited film formed on each of the substrates is locally annealed to relax the stress in the deposited film, and as a result, a deposited film with few defect and having good characteristics is formed on each of the substrates. In general, when the frequency of an electromagnetic wave for decomposing a raw material gas is increased, there is a tendency in that the energy of ion impinged in a substrate is decreased. For the reason for this, it is considered such that although damage of ion bombardment

to the substrate is slight, assistant energy by the ion which accelerates the surface mobility when the active species are deposited on the substrate is insufficient. For this reason, in order to improve the characteristics of the deposited film, even when the frequency of the electromagnetic wave to decompose the raw material gas is selected as above describe, there is an occasion in that the effect thereof is diminished depending on film-forming conditions adopted. This tendency becomes significant particularly under condition of a large deposition rate where the surface mobility is liable to become insufficient. According to the present invention, even under such condition, by applying the bias voltage to the cathode electrode to impart the energy to the ions as above described, under any condition, particularly even under the condition where the deposition rate is relatively large, the effect of improving the characteristics is obtained. In this case, the stability of the discharge can be confirmed by monitoring the change in the inner pressure or/and the luminance or the change in the bias current flown when the bias voltage is applied.

[0015]

And by rotating the rotary shaft 209 on which the substrate 205 is mounted by means of the motor 210 to rotate the substrate about the central axis in a generatrix direction of the substrate, a deposited film is uniformly formed on the entire surface of the substrate 205. When the film formation is conducted while rotating the substrate, the thickness of a deposited film formed on the substrate per one revolution of the substrate differs depending on a film deposition rate and a rotating speed of the substrate. In the film formation by overlapping the microwave and high

frequency having a specific frequency of the present invention, although depending on a ratio between the microwave power and the high frequency power introduced, by making the thickness of a deposited film formed on the substrate per one revolution of the substrate to be less than 2000 Å, there can be formed a deposited film having excellent characteristics on the substrate at a good reproducibility. The reason for this is considered such that an influence of a deposited film formed on a substrate surface oblique to the discharge space (said deposited film is corresponding to a slant face film: the characteristics thereof are liable to deteriorate in comparison with those of a front face film) [see, Japanese Unexamined Patent Publication Hei.1-127679] is diminished. The present inventor conducted experimental studies of said slant face film. As a result, there was obtained a finding that when the microwave and the high frequency are overlapped as in the present invention, as the proportion of the microwave power is increased, the influence of the slant face film is more liable to appear. (On the other hand, when the proportion of the microwave power is relatively small, the influence of the slant face film is small.) Specifically when the ratio of the microwave energy is 0.5 to 1.0, it is preferred that the thickness of a deposited film formed on the substrate per one revolution of the substrate is made to be less than 2000 Å.

[0016]

The formation of a second layer on the first layer thus formed is conducted by introducing raw material gas with a composition ratio which is different from that of the raw material gas used for the formation of the first layer into the reaction vessel 201 and

commencing glow discharge as well as in the formation of the first layer. At this time, it is not always necessary that the discharge in the reaction vessel 201 is once suspended and the inside of the reaction vessel is evacuated to a prescribed vacuum. It is possible that the discharge is not suspended but maintained by controlling a gas glow rate-controlling means (not shown) by a manual manner or a computer to gradually changing the gas composition for the formation of the first region to that for the formation of the second region. For example, when the first layer is formed by monosilane gas (100%) with 400 sccm, diboran gas (diluted to 3000 ppm with hydrogen gas) with 150 sccm and helium gas with 1000 sccm and the second layer is formed by monosilane gas (100%) with 200 sccm, diboran gas (diluted to 3000 ppm with hydrogen gas) with 10 sccm and helium gas with 2000 sccm, soon after the formation of the first layer, the flow rate of each raw material gas is changed to that for the formation of the second layer by MFC or the like. In the case where the kind of raw material gas is changed, it is possible that the flow rate of prescribed raw material gas is gradually decreased to zero or is gradually increased from 0 to a prescribed flow rate by way of control by means of MFC or the like. Specifically, for example, when a nc-Si:(H, X)layer as the first layer contains carbon atoms and the second layer comprises a nc-Si:(H, X)containing no carbon atoms, the flow rate of carbon atom-supplying raw material gas (for example, methane gas) is rapidly decreased to zero upon the termination of the formation of the first layer by means of MFC or the like. At this time, control of the flow rates of other raw material gases (such as monosilane gas, diboran gas, hydrogen gas, halogen atom-supplying gas, and

helium gas) than the carbon atom-supplying raw material gas can be changed as well as in the above case in accordance with the layer-forming conditions. On the other hand, when a nc-Si: (H, X)layer as the first layer contains no carbon atoms and the second layer comprises a nc-Si: (H, X) containing carbon atoms, the flow rate of carbon atom-supplying raw material gas (for example, methane gas) is rapidly increased until a prescribed flow rate starting from zero upon the termination of the formation of the first layer by means of MFC or the like.

【0017】

FIG. 3 schematically shows another constitution of the present invention, that is, an apparatus view of the type in that in the constitution of FIG. 2, the introduction position of the cathode electrode is changed and the cathode electrode serves also as the gas introduction pipe, and the number of the substrates is changed from 6 to 8. FIG. 3A is a schematic longitudinal section view, and FIG. 3B is a schematic cross-sectional view taken along the line X-X in FIG. 3A. In the figures, reference numeral 301 indicates a reaction vessel formed to have air-tight structure. Reference numeral 302 indicates a cathode electrode which serves also as a gas introduction pipe. The cathode electrode is electrically connected to a high frequency power source 304 capable of emitting an electromagnetic wave having a prescribed frequency of the present invention through a matching box 303. Reference numeral 315 indicates a direct current power source (a bias power source) for applying a direct current voltage to a bias electrode 302. The direct current power source is electrically connected to the cathode electrode as well as the high frequency power source. Reference

numeral 314 indicates a microwave introduction dielectric window comprising a material (for example, quartz glass, alumina ceramics, or the like) which is capable of efficiently transmitting a microwave power into the reaction vessel 301 and is capable to hermetically seal the inside of the reaction vessel. Reference numeral 313 indicates a waveguide for transmitting a microwave power. The waveguide comprises a rectangular portion extending from the microwave power source to the vicinity of the reaction vessel and a cylindrical portion which is inserted in the reaction vessel. The waveguide 313 is electrically connected to the microwave power source (not shown) together with a stub tuner (not shown) and an isolator (not shown). The dielectric window 314 is hermetically fixed to the inner wall of the cylindrical portion of the waveguide 313 so as to maintain the inside atmosphere of the reaction vessel in an enclosed state. Reference numeral 308 indicates an exhaust pipe which is open in the reaction vessel 301 through one end portion thereof and is communicated with an exhaustion device (not shown) through the other end portion thereof. In the reaction vessel 301, there are provided substrates 305, substrate holders 306, heaters 307 for heating the substrates. Reference numeral 312 indicates a discharge space which is circumscribed by the substrates 305. Reference numeral 309 indicates a rotary shaft capable of being rotated by a motor 310. The production of an electrophotographic photosensitive member using the fabrication apparatus of FIG. 3 can be conducted in accordance with the procedures described in the above with reference to FIG. 2.

[0018]

In the following, description will be made of an example of a light

receiving member prepared by the deposited film-forming apparatus and the deposited film-forming method of the present invention. FIG. 1 is a schematic view illustrating part of a layer constitution of an electrophotographic light receiving member formed by the method of the present invention. The electrophotographic light receiving member 100 formed by the present invention comprises a photoconductive layer 102 and a surface layer 103 sequentially formed on a substrate 101. The substrate 101 used in the present invention may comprise, for example, a metal such as Al, Cr, Mo, Au, In, Nb, Te, V, Ti, Pt, Pb, or Fe, or an alloy thereof such as stainless steel. Besides, synthetic resin films and sheets made of polyester, polystyrene, polycarbonate, cellulose acetate, polypropylene, polyvinyl chloride, or polyamide, and electrically insulating members made of glass or ceramics can be used as the substrate by subjecting their surfaces on which a photoconductive layer is to be formed to a electroconductive treatment. It is preferred that their opposite surfaces on which no photoconductive layer is to be formed are also applied with an electroconductive treatment. The substrate 101 may shaped in a cylindrical form or a plate-like endless belt form having a smooth flat surface or an irregular surface. The thickness thereof should be properly determined so that a desired electrophotographic light receiving member can be formed. In the case where an electrophotographic light receiving member to be obtained is required to have flexibility, the substrate can be made to be as thinner as possible within a range capable of exhibiting the function as the substrate. However, in view of the fabrication and handling or mechanical strength of the

substrate, the thickness is usually made to be more than 10 μm.

[0019]

In the present invention, it is possible to provide irregularities at the surface of the substrate 101. For example, in the case where image-recording is conducted using coherent light such as laser beam or the like, the substrate 101 may be designed to have un uneven surface in order to effectively prevent occurrence of defective images based on interference fringe patterns. The uneven surface may be an uneven pattern based on a plurality of spherical dimples. Specifically, the uneven surface of the substrate in this case may comprise a plurality of minute irregularities having a magnitude which is smaller than the resolution power required for the electrophotographic photosensitive member, where the irregularities are based on a plurality of spherical dimples. By this, it is possible to obtain a more fine image even in the case of using coherent light. In the present invention, the photoconductive layer 102 is formed of a non-single crystal material having desired characteristics by means of a plasma CVD process in which the microwave with a frequency of 2.45 GHz and the electromagnetic wave with a frequency of 20 MHz to 450 MHz are overlapped, and if necessary, a bias voltage is applied to the cathode electrode. Specifically, for example, in order to form a photoconductive layer 102 comprising a-Si, basically a raw material gas capable of supplying silicon atoms (Si) in a desired gaseous state is introduced into the reaction vessel whose inside is capable of being depressurized, in the reaction vessel, the microwave with a frequency of 2.45 GHz and the electromagnetic wave with a frequency of 20 MHz to 450 MHz are used, if necessary,

a bias voltage is applied to the cathode electrode, whereby glow discharge is generated to form a layer comprising a-Si on a substrate 101 previously arranged at a prescribed position. However, it is a point of the present invention that the introduction time of the microwave is differentiated from that of the high frequency.

[0020]

In the present invention, it is effective to introduce atoms of an element capable of controlling conductivity into the photoconductive layer 102. It is also effective to introduce atoms of halogen element such as fluorine as a modifying material, if necessary, also atoms of carbon, nitrogen, or oxygen. In order to form the photoconductive layer 102 comprising a-Si capable of achieving the object of the present invention, it is necessary that the substrate temperature and the gas pressure in the reaction vessel are controlled as required. For the substrate temperature (Ts), an optimum range should be determined in accordance with the layer design. However, in general, it is desired to be preferably in a range of 20 to 500 ℃, more preferably in a range of 50 to 480 ℃, most preferably in a range of 100 to 450 ℃. Similarly, also for the gas pressure in the reaction vessel, an optimum range should be determined in accordance with the layer design. However, in general, it is desired to be preferably in a range of 1×10^{-5} to 100 Torr, more preferably in a range of 5×10^{-5} to 30 Torr, most preferably in a range of 1×10^{-4} to 10 Torr.
In the present invention, as the preferred numerical range of the substrate temperature and that of the gas pressure in the reaction vessel in order to form the photoconductive layer, aforesaid ranges

can be mentioned. However, these layer-forming factors should not be independently decided. It is desired that optimum values of the layer region-forming factors are decided on the basis of the mutual and organic relationships in order to form a light receiving member having desired characteristics. In the present invention, the thickness of the photoconductive layer should be determined having a due care so that desired electrophotographic characteristics are obtained and also in view of economical advantage. However, in general, it is preferably in a range of 5 to 50 μm, more preferably in a range of 10 to 40 μm, most preferably in a range of 15 to 30 μm. Further in the present invention, it is preferred that the photoconductive layer 102 is made have a layer region on the substrate side, containing at least aluminum atoms, silicon atoms and hydrogen atoms in an unevenly distributed state. Similarly, it is possible for the photoconductive layer to contain halogen atoms or atoms of carbon, nitrogen or oxygen in a uniformly or unevenly distributed state. Besides, it is possible that the photoconductive layer is functionally divided to comprise a charge transportation layer and a charge generation layer.

【0021】

The surface layer 103 in the present invention is formed of a non-single crystal material having desired physical characteristics, electric characteristics and resistance to environment by means of a plasma CVD process in which the microwave with a frequency of 2.45 GHz and the electromagnetic wave with a frequency of 20 MHz to 450 MHz are overlapped, and if necessary, a bias voltage is applied to the cathode electrode. In the present invention, it is effective to introduce atoms of an

element capable of controlling the conductivity into the surface layer. Specifically, for example, in the case of forming a surface layer comprising an amorphous silicon carbide (a-SiC), basically a silicon atoms (Si)-containing raw material gas and a carbon atoms (C)-containing raw material gas are introduced into the reaction vessel whose inside is capable of being depressurized, in the reaction vessel, the microwave with a frequency of 2.45 GHz and the electromagnetic wave with a frequency of 20 MHz to 450 MHz are overlapped, if necessary, a bias voltage is applied to the cathode electrode, whereby glow discharge is generated to form a deposited film on the substrate having the photoconductive layer previously formed thereon. Also in this case, it is a point of the present invention that the introduction time of the microwave is differentiated from that of the high frequency. In the present invention, the thickness of the surface layer 103 should be determined having a due care so that desired electrophotographic characteristics are obtained and also in view of economical advantage. However, in general, it is preferably in a range of 0.01 to 30 μm, more preferably in a range of 0.05 to 20 μm, most preferably in a range of 0.1 to 10 μm. Besides, the power of the electromagnetic wave with a frequency of a VHF band region which is applied to decompose the raw material gas is preferred to be generally 10 to 5000 W or preferably 20 to 2000 W, respectively per one substrate.

[0022]

In the present invention, as the preferred numerical range of the substrate temperature and that of the gas pressure in the reaction vessel in order to form the surface layer, aforesaid ranges can be

mentioned. However, these layer-forming factors should not be independently decided. It is desired that optimum values of the layer region-forming factors are decided on the basis of the mutual and organic relationships in order to form a light receiving member having desired characteristics. In the present invention, it is possible to provide a region at an interface portion between the photoconductive layer and the surface layer such that the characteristics of the composition or the like are continuously changed from the photoconductive layer to the surface layer. The thickness of this region is made to be such that forms a substantial interface between the photoconductive layer and the surface layer. The region is not meant a so-called interface-less state which gently connects between the conductive layer and the surface layer such that the interface cannot be specified with respect to the composition and the characteristics. Besides, in the layer constitution of the electrophotographic light receiving member formed according to the present invention, it is possible to provide a contact layer, a lower charge injection inhibition layer, or the like if necessary in order to have desired characteristics as the electrophotographic light receiving member. When these layers are provided, it is possible to provide a region between the adjacent layers such that the composition or the like are continuously changed. The thickness of this region is of an extent which substantially forms an interface.

[0023]

As specific preferable examples of the Si-supplying raw material gas used in the present invention, there can be mentioned gaseous or easily gasifiable silicon hydrides (silanes) such as SiH_4,

Si_2H_6, Si_3H_8, Si_4H_{10}, and the like. Of these, SiH_4 and Si_2H_6 are particularly preferred in view of the easy layer forming work and the good efficiency for the supply of Si. Besides the silicon hydrides, there can be also mentioned fluorine-containing silicon compounds, namely, fluorine-substituted silane derivatives. Specific examples are gaseous or easily gasifiable silicon fluorides such as SiF_4, Si_2F_6, and the like, and gaseous or easily gasifiable fluorine-substituted silicon hydrides such as SiH_3F, SiH_2F_2, $SiHF_3$, and the like. If necessary, these Si-supplying raw material gases may be used while being diluted with appropriate gas such as H_2 gas, He gas, Ar gas, or Ne gas. The carbon atoms (C)-supplying raw material gas can include hydrocarbons comprising carbon atoms and hydrogen atoms such as saturated hydrocarbons of 1 to 5 carbon atoms, ethylene series hydrocarbons of 2 to 4 carbon atoms, and acetylene series hydrocarbons of 2 to 3 carbon atoms. Specific examples of such saturated hydrocarbon are methane (CH_4), ethane (C_2H_6), propane (C_3H_8), n-butane (n-C_4H_{10}), and pentane(C_5H_{12}); specific examples of such ethylene series hydrocarbon are ethylene(C_2H_4), propylene (C_3H_6), butene-1(C_4H_8), butene-2 (C_4H_8), isobutylene (C_4H_8), and pentene (C_5H_{10}); and specific examples of such acetylene series hydrocarbon are acetylene (C_2H_2), methylacetylene (C_3H_4), and butyne (C_4H_6). Besides, carbon fluorides such as CF_4, CF_3, C_2F_6, C_3F_8, and C_4F_8 are also usable as the C-supplying raw material gas. The nitrogen atoms (N)-supplying raw material gas can include nitrogen compounds such as nitrogen gas (N_2), nitrogen nitrides and azides comprising nitrogen and hydrogen atoms such as NH_3, H_2NNH_2, HN_3, and NH_4N_3 which are gaseous or easily gasifiable. Besides, there can be mentioned halogenated

nitrogen compounds such as NF_3, N_2F_4, and the like which are capable of supplying nitrogen atoms together with halogen atoms. The oxygen atoms (O)-supplying raw material gas can include O_2,O_3, NO, NO_2, N_2O, N_2O_3, N_2O_4, N_2O_5, and NO_3. Besides, lower siloxanes containing silicon (Si), oxygen (O) and hydrogen (H) atoms as the constituent atoms such as $H_3SiOSiH_3$, $H_3SiOSiH_2OSiH_3$, and the like can be mentioned. These raw material gases may be used while being diluted with appropriate gas such as H_2 gas, He gas, Ar gas, or Ne gas. It is possible to use an alkyl silicide such as $Si(CH_3)_4$ or $Si(C_2H_5)_4$ in addition to any of the foregoing raw material gases. The raw material gases used in the present invention may be supplied separately from different supply sources (bombs). It is also possible to use them by mixing them at a prescribed mixing ratio.

[0024]

As described in the above, in the present invention, the two different electromagnetic waves having a different frequency are separately introduced while differentiating the introduction time of one electromagnetic wave from that of the other electromagnetic wave and specifying the frequency of each of the electromagnetic waves, whereby repeatability of the stability and uniformity of the plasma state at an initial stage of the discharge are achieved while the characteristics of a deposited film formed at an initial stage of the discharge are improved, and by virtue of the overlapping effect of the electromagnetic waves having a different frequency which are introduced as above described, a deposited film is formed at an adequate deposition rate, whereby a deposited film having excellent characteristics is formed. The reason for this is considered such that will be described in the following. The

time since the time when the first electromagnetic wave having a first frequency is introduced until the second electromagnetic wave having a second frequency is introduced is excessively short, the effect of the present invention is not exhibited. And when said time is excessively long, problems will entail such that the deposited film formed only by the first electromagnetic wave having a first frequency has a thickness of a certain extent and the deposited film formed thereon by the second electromagnetic wave having a second frequency overlapped in addition to the first electromagnetic wave having a first frequency has a structure which is different from that of the first formed deposited film, where a structural stress is liable to occur at an interfacial portion of the stacked deposited film comprising the two deposited films having a different structure which are stacked, and as a result, a light receiving member comprising such deposited film is inferior in terms of the characteristics, and the light receiving member is apt to suffer peeling at the interfacial portion. Therefore, although the introduction time of the first electromagnetic wave having a first frequency and that of the second electromagnetic wave having a second frequency are different depending on the inner pressure, the substrate temperature, the deposition rate, or the energy introduced upon the formation of the deposited film, it is appropriate in the present invention that the second electromagnetic wave having a second frequency is introduced preferably within 1 second to 10 minutes since the time when the first electromagnetic wave having a first frequency is introduced, more preferably within 0.05 second to 5 minutes since the time when the discharge generated by the first

electromagnetic wave having a first frequency is stabilized, most preferable within 0.01 second to 3 minutes since the time when the discharge generated by the first electromagnetic wave having a first frequency is stabilized. The stabilization of the discharge can be recognized by monitoring a change in the inner pressure or/and the luminance from the commencement of the discharge. That is, at a stage soon after the discharge is commenced, the energy of the high frequency is also not stabilized (at an initial state of the discharge, the energy which is greater than the discharge-maintaining power is required), and because of this, the inner pressure upon the decomposition of the raw material gas or/and the number of the luminescent species generated are greatly changed. When the discharge is stabilized, the change rates of theses are diminished.

[0025]

As above described, in the case where a deposited film is formed by means of a plasma CVD process, the plasma state at an initial state of the discharge greatly influences to the characteristics of a deposited film formed. The reason for this is considered as follows. In general, upon the commencement of the discharge, the energy which is greater than that to maintain the discharge in a steady state is required. The discharge is meant a phenomenon in that a small amount of electrons present in air are accelerated by an electromagnetic wave to collide with the molecules of the air thereby to increase the kinetic energy of the molecules and the inner energy of the molecules, whereby the molecules are excited, dissociated, and ionized to produce plasma comprising active species which are present while maintaining a certain density, where the

numbers of electrons, ions, and the like which are generated and those of electrons, ions, and the like which are extinguished are balanced. In view of this, upon generating discharge to produce plasma, it is necessary to supply an energy capable of generating large quantities of electrons, ions, and the like against the numbers of the electrons, the ions, and the like which are extinguished. On the other hand, when the discharge which is once generated is maintained, it is sufficient to supply an energy necessary to generate electrons and ions which supplement the electrons and ions which are extinguished. Therefore, upon commencing the discharge, it is necessary to supply an energy which is greater than that required to maintain the discharge in a steady state. Thus, when the state of the plasma at the initial state of the discharge is compared with that when the discharge is in a steady state, they delicately differ one from the other.

[0026]

Also at the initial stage of the discharge, a deposited film of a certain extent is formed on the substrate. There is an occasion in that the deposited film formed at the initial stage of the discharge and that formed when the discharge is in the steady state are structurally different. And a deposited film is directly formed on the substrate at the initial stage of the discharge and thereafter, a deposited film is formed on the deposited film previously formed. Therefore, there is a tendency in that the structural difference between them becomes significant. Particularly, when two different electromagnetic waves having a different frequency are simultaneously introduced, the electric field is complicated, where it becomes difficult to control the

electrons and ions during the time until the discharge becomes to be in a steady state. Because of this, there is a tendency in that the deposited film formed at the initial stage of the discharge is inferior in terms of the characteristics. There is a tendency in that the characteristics of such deposited film formed at the initial stage of the discharge (that is, the deposited film directly formed on the substrate) greatly influence to the electrical matching property with the substrate, that is, influence to the electric characteristics between the deposited film and the substrate. In corresponding to the inferior characteristics of the deposited film formed at the initial stage of the discharge, there will entail a variation among the lots in terms of the characteristics. Such initial discharge is liable to become uneven, resulting in a variation among the light receiving members in the same lot or a positional variation for one light receiving member respectively in terms of the characteristics.

[0027]

Therefore, in the present invention, for the two different electromagnetic waves having a different frequency which are introduced, by differentiating their introduction times at a prescribed period of time, the frequency of the electromagnetic wave which is introduced upon commencing the discharge is singled. By this, the unstable factor of the plasma state upon commencing the discharge is eliminated to make it possible to stably form a deposited film having excellent characteristics. Together with this, after elapse of a prescribed period of time, by introducing the other electromagnetic wave having a different frequency to overlap with the previously introduced electromagnetic wave, the

power introduced is optimized, whereby the performance of decomposing the raw material gas and/or the energy of the active species after the decomposition of the raw material gas are optimally controlled to improve the film deposition rate thereby to make it possible to stably form a deposited film having excellent characteristics. Particularly, as above described, in the present invention, after elapse of a prescribed period of time since the first electromagnetic wave having a first frequency is introduced, the second electromagnetic wave having a second frequency is introduced, by stable and uniform plasma by the single electromagnetic wave at the initial stage of the discharge, a deposited film having excellent characteristics is formed at good repeatability, and by the overlapping of the second electromagnetic wave having a second frequency, a deposited film is formed at an adequate deposition rate.

[0028]

In the following, the present invention will be described in more detail with reference to experiments and examples. It should be understood that the scope of the present invention is not restricted by these experiments and examples.

[Experiments]

(Experiment 1)

In order to examine changes in the deposition rate of a deposited film deposited when the microwave and the high frequency are overlapped, the following experiment was conducted. As shown in Table 1, the microwave and the high frequency were variously combined. Using each combination and varying the microwave power, on a substrate comprising an aluminum cylinder having a

mirror-ground surface and which has been degreased and washed, there was formed a deposited film under conditions shown in Table 2 and in accordance with the deposited film-forming procedures. Based on the resultants, there were obtained film-deposition rates, and the resultant film-deposition rates were compared. In the above, in the conditions shown in Table 2, the high frequency energy introduced was fixed at a value corresponding to 50% of the energy with which the deposition rate was saturated, and the power of the microwave was varied. The results obtained are shown in Table 3. Here, the values shown in this table are relative values when the deposition rate in the case where no microwave was introduced is set at 1. As the results of Table 3 illustrate, it is understood that by overlapping the microwave with the high frequency, the deposition rate of the deposited film is markedly improved. In addition, as a result of having conducted similar experiments by varying the power of the high frequency, for any of the cases where the deposition rate is not saturated by the high frequency, it was confirmed that the deposition rate is improved by overlapping the microwave, as well as in the above.

[0029]

(Experiment 2)

In order to examine variation relations with respect to the characteristics of an electrophotographic light receiving member prepared by differentiating the introduction time of the microwave and that of the high frequency, the following experiment was conducted.

(1) Using the fabrication apparatus shown in FIG. 2, on a substrate comprising an aluminum cylinder having a

mirror-ground surface and which has been degreased and washed, there was formed a deposited film comprising a photoconductive layer and a surface layer by overlapping the microwave with a frequency of 2.45 and the high frequency with a frequency of 20 MHz to 450 MHz in the same manner as in Experiment 1 and under conditions shown in Table 4 to obtain an electrophotographic light receiving member having such configuration as shown in FIG. 1 (the electrophotographic light receiving member will be hereinafter referred to as drum). In the above, after elapse of a prescribed period of time since the introduction of the high frequency, the microwave was introduced. As the cathode electrode, there was used a cylindrical cathode electrode having a diameter of 30 mm. As the substrate, there were used a plurality of cylindrical aluminum cylinders having a diameter of 80 mm, a length of 358 mm, and a thickness of 5 mm. This operation was repeated 100 times for each combination to obtain 100 lots comprising a plurality of drums. Each of the drums was set to a modification of an electrophotographic apparatus NP 6060 produced by CANON Kabushiki Kaisha (modified for experimental purposes), where endurance test in which copying shot by an electrophotographic image-forming process is continuously performed 1000000 times was conducted, after the endurance test, evaluation was conducted with respect to ghost appearance, blanc exposure memory, charge retentivity unevenness, photosensitivity unevenness, smeared image appearance, fine-line reproduction, white dot appearance, and black dot appearance as will be described below. The evaluated results of these evaluation items were compared for each lot to examine reproducibility of the characteristics. And the results were

categorized on the basis of the following criteria.

◎ : particularly good

○ : good

△ : the characteristics are varied but they meet the product standard

X : the characteristics are greatly varied and they do not meet the product standard

The evaluation of each of the foregoing evaluation items was performed in the following manner.

Ghost Appearance: The evaluation of ghost appearance was performed in the following manner. A ghost test chart FY9-9040 produced by CANON Kabushiki Kaisha having a black solid circle with a reflection density of 1.1 and having a diameter of 5 mm fixed thereto is placed on the original table and a halftone test chart produced by CANON Kabushiki Kaisha is superposed on the ghost test chart, followed by subjecting to reproduction to obtain a copied image. A difference between the reflection density of the black circle with a diameter of 5 mm observed on the copied halftone and that of the copied halftone portion is examined.

Blank Exposure Memory: The evaluation of blank exposure memory was performed in the following manner. A halftone test chart FY9-9042 produced by CANON Kabushiki Kaisha is placed on the original table, followed by subjecting to reproduction to obtain a copied image. Having attention to a portion of the copied image which is corresponding to a portion of the surface of the drum having been irradiated with blank exposure, a difference between the reflection density of the portion irradiated with no blank exposure and that of the portion irradiated with the blank exposure

is examined.

Charge Retentivity Unevenness: The evaluation with respect to charge retentivity unevenness was performed in the following manner. The drum is set to the electrophotographic apparatus. Corona charging is performed by applying a high voltage of +6 kV to the charger, where the surface potential in dark of the drum is measured by a surface potentiometer, particularly, the surface potential is measured for a plurality of portions of the drum at an interval of 3 cm from the top to the bottom. For the measured surface potentials, an average value is obtained. The average value is made to be a charge retentivity for the drum. And the value of the measured potential which is the most remote from the average value is made to be a charge retentivity unevenness for the drum. The drums obtained in one film formation lot are evaluated in the above-described manner. Of the drums, the one which was concluded to be the worst in terms of charge retentivity unevenness was evaluated on the basis of the criteria which will be described later.

Photosensitivity Unevenness: The evaluation with respect to photosensitivity unevenness was performed in the following manner. The drum is set to the electrophotographic apparatus. The drum is charged to have a prescribed surface potential in dark, followed by irradiating photo image. The irradiation of the photo image is performed by irradiating light excluding a light having a wavelength of less than 550 nm using a Xenon lump light source and a filter. At this time, for the drum involved, its surface potential in light is measured by a surface potentiometer. And the quantity of exposure is adjusted so that the surface potential

in light becomes to be a prescribed potential, where the exposure quantity is made to be a photosensitivity for the drum. This measurement procedure is performed for a plurality of portions of the drum at an interval of 3 cm from the top to the bottom. For the measured photosensitivity values, an average value is obtained. The average value is made to be an average photosensitivity for the drum. And the measured photosensitivity value which is most remote from the average photosensitivity is made to be a photosensitivity unevenness for the drum. The drums obtained in one film formation lot are evaluated in the above-described manner. Of the drums, the one which was concluded to be the worst in terms of photosensitivity unevenness was evaluated on the basis of the criteria which will be described later.

Smeared Image Appearance: The evaluation with respect to smeared image appearance was performed in the following manner. A test chart FY9-9058 produced by CANON Kabushiki Kaisha having characters in the entire white back ground is placed on the original table, where exposure with an quantity which is 2 times ordinary exposure quantity is performed to obtain a copied image. For the copied image, whether or not the fine lines are continued without being disconnected is optically examined in four steps. When uneven portions are present on the copied image, the evaluation is performed of the portion which is the worst in the entire area.

White Dot Appearance: The evaluation with respect to white dot appearance was performed in the following manner. A whole black test chart FY9-9073 produced by CANON Kabushiki Kaisha is placed on the original table, where a copied image is obtained. For the copied image, the number of white dots with a diameter of less than 0.2

mm which are present in a selected area is examined.

Black Dot Appearance: The evaluation with respect to white dot appearance was performed in the following manner. 10 white copying papers are placed on the original table while being piled, where a copied image is obtained. For the copied image, the number of black dots with a diameter of less than 0.2 mm which are present in a selected area is examined.

The evaluated results obtained in the above are shown in Table 5.

(2) In the (1) of Experiment 2, except for introducing the microwave after elapse of a prescribed period of time since the time when the discharge by the high frequency was generated, the reproducibility of the characteristics was examined by performing comparison for every lot in the same manner. The results are shown in Table 6.

(3) In the (1) of Experiment 2, except for introducing the microwave after elapse of a prescribed period of time since the time when the discharge by the high frequency was generated and the discharge was stabilized , the reproducibility of the characteristics was examined by performing comparison for every lot in the same manner. At this time, the stabilization of the discharge was to be the time when the change rate of the luminance/the inner pressure during the discharge became to be within 5%. The results are shown in Table 7. The results shown in Tables 5 to 6 illustrate, the following facts are understood. That is, when the microwave is introduced within a time of 1 second to 10 minutes since the time when the high frequency is introduced, the effect of the present invention is exhibited. When the microwave is introduced within a time of 0.05 second to 5 minutes since the time when the discharge by the high

frequency is generated, the effect of the present invention becomes significant. When the microwave is introduced within a time of 0.01 second to 3 minutes since the time when the discharge by the high frequency is generated and the discharge is stabilized, the effect of the present invention becomes more significant. Separately, as a result of having repeated the procedures of (1) to (3) of Experiment 2 by changing the introduction order of the high frequency and the microwave, similar results were obtained.

【0031】

(Experiment 3)

In order to examine the interrelations of the introduction power of the high frequency and that of the microwave and also the ratio between the two powers to the characteristics of the drums obtained, the following experiment was conducted. Particularly, the procedures of Experiment 2 were repeated under conditions shown in Table 4 while changing the introduction power of the high frequency and that of the microwave and also the ratio between the two powers, whereby a plurality of drums were prepared.

(1) The frequency of the high frequency was fixed at 105 MHz. In the conditions shown in Table 4, the introduction power thereof and the power of the microwave were changed so that the deposition rate became to fall in a range of 10% to 200% of the energy with which the deposition rate is saturated. The resultant drums were evaluated in the same manner as in Experiment 2, and judgment was performed on the basis of the following criteria.

With respect to ghost appearance:

◎: particularly good, ○: good, △: not problematic in practice, and X: problematic in practice.

With respect to blank memory:

◎: particularly good, ○: good, △: not problematic in practice, and X: problematic in practice.

With respect to charge retentivity unevenness:

◎: particularly good, ○: good, △: not problematic in practice, and X: problematic in practice.

With respect to photosensitivity unevenness:

◎: particularly good, ○: good, △: not problematic in practice, and X: problematic in practice.

With respect to smeared image appearance:

◎ : good, ○ : partial disconnection is present, △ : many disconnections are present but the characters can be recognized and they are acceptable in practice, and X: many disconnections are present so that the characters cannot be recognized and they are unacceptable in practice.

With respect to white dot appearance:

◎: particularly good, ○: good, △: not problematic in practice, and X: problematic in practice.

With respect to black dot appearance:

◎: particularly good, ○: good, △: not problematic in practice, and X: problematic in practice.

The results are shown in Tables 2 to 14. As the results shown in these tables illustrate, the following facts are understood. That is, when the high frequency energy is singly introduced, the deposition rate is less than 150% of the energy with which the deposition rate is saturated, and when the ratio of the microwave energy/the high frequency energy is in a range of 0.05 to 2.0, the effect of the present invention becomes significant.

(2) Experiment was conducted by repeating the procedures of the (1) of Experiment 3, except for changing the frequency of the high frequency in a range of 20 MHz to 450 MHz. As a result, there were obtained the following findings. That is, when the high frequency energy is singly introduced, the deposition rate is less than 150% of the energy with which the deposition rate is saturated, and when the ratio of the microwave energy/the high frequency energy is in a range of 0.05 to 2.0, the effect of the present invention becomes significant.

(3) In the (1) and the (2) of Experiment 3, the interrelations between the microwave power and the energy with which the deposition rate is saturated were examined. As a result, the following finding was obtained. That is, as well as the high frequency, the effect of the present invention becomes significant when the microwave power is less than 150% of the energy with which the deposition rate is saturated.

The significancy of the effect of the present invention is apparent from the results of the above experiments. However, the advantages and features of the present invention will be described in more detail with reference to examples and comparative examples. It should be understood that these examples are only for illustrative purposes and are not intended to restrict the scope of the present invention.

【0032】

【Examples and Comparative Examples】

[Example 1]

Using the fabrication apparatus shown in FIG. 2 and in accordance with the procedures of Experiment 2, there were prepared a

plurality of electrophotographic light receiving drums having such configuration as shown in FIG. 4 by sequentially forming a charge injection inhibition layer, a photoconductive layer and a surface layer on each of a plurality of substrates each comprising an aluminum cylinders having a mirror ground surface and having been degreased and washed under conditions shown in Table 15. At this time, the frequency of the high frequency was fixed at 105 MHz, and under the conditions shown in Table 15, the introduction power was made to be 50% of the energy with which the deposition rate is saturated, and the ratio of the microwave energy/the high frequency energy was made to be 0.8. For the introduction time of the high frequency and that of the microwave, after elapse of 0.5 second since the time when the high frequency was introduced to generate plasma and the plasma was stabilized, the microwave was introduced. The cathode electrode was made to comprise a cylindrically shaped cathode electrode having a diameter of 30 mm. As said plurality of aluminum cylinders as the substrates, there were used 6 cylindrical aluminum cylinders having a diameter of 80 mm, a length of 358 mm and a thickness of 5 mm. Under this condition, the above fabrication operation was repeated 100 times to obtain 100 lots each comprising 6 electrophotographic light receiving drums. Each of the resultant drums was set to a modification of an electrophotographic apparatus NP 6060 produced by CANON Kabushiki Kaisha (modified for experimental purposes), where as well as in Experiment 2, endurance test in which copying shot by an electrophotographic image-forming process is continuously performed 1000000 times was conducted, after the endurance test, evaluation was conducted with respect to ghost

appearance, blanc exposure memory, charge retentivity unevenness, photosensitivity unevenness, smeared image appearance, white dot appearance, and black dot appearance. The results obtained are shown in Table 16.

(Comparative Example 1)

The procedures of Example 1 were repeated, except that the high frequency and the microwave were introduced at the same time in order to examine the effect of the introduction time for the high frequency and the microwave, to obtain a plurality of drums. The resultant drums were evaluated in the same manner as in Example 1. The results obtained are shown in Table 16 together with the evaluated results obtained in Example 1.

(Comparative Example 2)

The procedures of Example 1 were repeated, except that after elapse of 15 minutes since the introduction of the high frequency, the microwave was introduced in order to examine the effect of the introduction time for the high frequency and the microwave, to obtain a plurality of drums. The resultant drums were evaluated in the same manner as in Example 1. The results obtained are shown in Table 16 together with the evaluated results obtained in Example 1 and the evaluated results obtained in Comparative Example 1.

(Comparative Example 3)

The procedures of Example 1 were repeated, except that the ratio of the microwave energy/the high frequency energy was made to be 3.0 in order to examine the effect of the ratio between the introduction power of the high frequency and that of the microwave, to obtain a plurality of drums. The resultant drums were evaluated in the same manner as in Example 1. The results obtained are shown

in Table 16 together with the evaluated results obtained in Example 1 and the evaluated results obtained in Comparative Examples 1 and 2.

(Comparative Example 4)

The procedures of Example 1 were repeated, except that the ratio of the microwave energy/the high frequency energy was made to be 0.05 in order to examine the effect of the ratio between the introduction power of the high frequency and that of the microwave, to obtain a plurality of drums. The resultant drums were evaluated in the same manner as in Example 1. The results obtained are shown in Table 16 together with the evaluated results obtained in Example 1 and the evaluated results obtained in Comparative Examples 1, 2 and 3.

(Comparative Example 5)

The procedures of Example 1 were repeated, except that the frequency of the high frequency was made to be 13.56 MHz in order to examine the effect of the frequency, to obtain a plurality of drums. The resultant drums were evaluated in the same manner as in Example 1. The results obtained are shown in Table 16 together with the evaluated results obtained in Example 1 and the evaluated results obtained in Comparative Examples 1, 2, 3 and 4.

As the results shown in Table 16 illustrate, it is understood that by making the deposited film-forming conditions to those specific conditions established by the present invention, the effect of the present invention first becomes significant.

[0033]

[Example 2]

Using the fabrication apparatus shown in FIG. 2 and in accordance

with the procedures of Experiment 2, there were prepared a plurality of electrophotographic light receiving drums having such configuration as shown in FIG. 5 by sequentially forming a charge injection inhibition layer, a charge transportation layer, a charge generation layer and a surface layer on each of a plurality of substrates each comprising an aluminum cylinders having a mirror ground surface and having been degreased and washed under conditions shown in Table 17. At this time, the frequency of the high frequency was fixed at 105 MHz, and under the conditions shown in Table 17, the introduction power was made to be 50% of the energy with which the deposition rate is saturated, and the ratio of the microwave energy/the high frequency energy was made to be 0.8. For the introduction time of the high frequency and that of the microwave, after elapse of 0.5 second since the time when the high frequency was introduced to generate plasma and the plasma was stabilized, the microwave was introduced. The cathode electrode was made to comprise a cylindrically shaped cathode electrode having a diameter of 30 mm. As said plurality of aluminum cylinders as the substrates, there were used 6 cylindrical aluminum cylinders having a diameter of 80 mm, a length of 358 mm and a thickness of 5 mm. Under this condition, the above fabrication operation was repeated 100 times to obtain 100 lots each comprising 6 electrophotographic light receiving drums. Each of the resultant drums was set to a modification of an electrophotographic apparatus NP 6060 produced by CANON Kabushiki Kaisha (modified for experimental purposes), where as well as in Experiment 2, endurance test in which copying shot by an electrophotographic image-forming process is continuously performed 1000000 times

was conducted, after the endurance test, evaluation was conducted with respect to ghost appearance, blanc exposure memory, charge retentivity unevenness, photosensitivity unevenness, smeared image appearance, white dot appearance, and black dot appearance. The results obtained are shown in Table 18.

(Comparative Examples 6-10)

In Example 2, as well as in Comparative Examples 1 to 5, the introduction time for the high frequency and the microwave, the ratio of the two introduction powers, and the frequency of the high frequency were variously changed, and comparisons were performed. The results obtained are shown in Table 18 together with the results obtained in Example 1.

【0034】

[Example 3]

Using the fabrication apparatus shown in FIG. 2 and in accordance with the procedures of Experiment 2, there were prepared a plurality of electrophotographic light receiving drums having such configuration as shown in FIG. 6 by sequentially forming a photoconductive region 1, a photoconductive region 2 and a surface layer on each of a plurality of substrates each comprising an aluminum cylinders having a mirror ground surface and having been degreased and washed under conditions shown in Table 19. At this time, the frequency of the high frequency was fixed at 105 MHz, and under the conditions shown in Table 17, the introduction power was made to be 50% of the energy with which the deposition rate is saturated, and the ratio of the microwave energy/the high frequency energy was made to be 0.8. For the introduction time of the high frequency and that of the microwave,

after elapse of 0.5 second since the time when the high frequency was introduced to generate plasma and the plasma was stabilized, the microwave was introduced. The cathode electrode was made to comprise a cylindrically shaped cathode electrode having a diameter of 30 mm. As said plurality of aluminum cylinders as the substrates, there were used 6 cylindrical aluminum cylinders having a diameter of 80 mm, a length of 358 mm and a thickness of 5 mm. Under this condition, the above fabrication operation was repeated 100 times to obtain 100 lots each comprising 6 electrophotographic light receiving drums. Each of the resultant drums was set to a modification of an electrophotographic apparatus NP 6060 produced by CANON Kabushiki Kaisha (modified for experimental purposes), where as well as in Experiment 2, endurance test in which copying shot by an electrophotographic image-forming process is continuously performed 1000000 times was conducted, after the endurance test, evaluation was conducted with respect to ghost appearance, blanc exposure memory, charge retentivity unevenness, photosensitivity unevenness, smeared image appearance, white dot appearance, and black dot appearance. The results obtained are shown in Table 20.

(Comparative Examples 11-15)

In Example 3, as well as in Comparative Examples 1 to 5, the introduction time for the high frequency and the microwave, the ratio of the two introduction powers, and the frequency of the high frequency were variously changed, and comparisons were performed. The results obtained are shown in Table 20 together with the results obtained in Example 3. As the results shown in Tables 18 and 20 illustrate, it is understood that the present

invention is effective without depending on the layer constitution of the drum.

[0035]

[Example 4]

The procedures of each of Examples 1 to 3 were repeated, except that the frequency of the high frequency was changed to 20 MHz, 51 MHz, 105 MHz, and 250 MHz, to obtain a plurality of drums. The resultant drums were evaluated as well as in Examples 1 to 3 and Comparative Examples 1 to 15. As a result, there were obtained similar results.

[Example 5]

The procedures of each of Examples 1 to 3 were repeated, except that the introduction time of the microwave frequency since the introduction of the high frequency was changed to 0.01 second, 10 seconds, 60 seconds, and 180 seconds, to obtain a plurality of drums. The resultant drums were evaluated as well as in Examples 1 to 3 and Comparative Examples 1 to 15. As a result, there were obtained similar results.

[Example 6]

The procedures of each of Examples 1 to 3 were repeated, except that the introduction order of the high frequency and the microwave was reversed, to obtain a plurality of drums. The resultant drums were evaluated as well as in Examples 1 to 3 and Comparative Examples 1 to 15. As a result, there were obtained similar results.

[Example 7]

The procedures of each of Examples 1 to 3 were repeated, except that the fabrication apparatus was changed to the fabrication

apparatus shown in FIG. 3, to obtain a plurality of drums. The resultant drums were evaluated as well as in Examples 1 to 3 and Comparative Examples 1 to 15. As a result, there were obtained similar results.

[0036]

[Advantages of the invention] In the present invention, upon introducing at least two different electromagnetic waves having a prescribed different frequency into the reaction chamber, by introducing the electromagnetic wave having a second frequency after elapse of a prescribed period of time since the time when the electromagnetic wave having a first frequency, it is possible to stabilize and uniform the plasma at the initial stage of the discharge by single electromagnetic wave, where this situation makes it possible to form a deposited film having excellent characteristics at good reproducibility; and by way of the overlapping of the electromagnetic wave having a second frequency to the previously introduced electromagnetic wave, it is possible to form a deposited film at an adequate deposition rate, whereby a deposited film having excellent characteristics can be formed. Therefore, when this method is adopted, for instance, in the production of an electrophotographic photosensitive member, it is possible to efficiently mass-produce electrophotographic photosensitive members having uniform and excellent electrophotographic characteristics without causing ghost appearance, blank memory, charge retentivity unevenness, and photosensitivity unevenness and which reproduce high quality images without having image defects such as white dot appearance, black dot appearance, and the like.

[0037]

Further, in the present invention, by introducing the two different electromagnetic waves having a prescribed different frequency at the optimum time as above described, the plasma state at the initial stage of the discharge which is greatly influenced particularly to the characteristics of a deposited film formed can be stabilized to form a deposited film having excellent characteristics. In addition, in the present invention, by adopting a manner of introducing the two different electromagnetic waves having a prescribed different frequency respectively through a different introduction means, each power can be readily controlled as desired. Particularly, by introducing the microwave energy through the waveguide and introducing the high frequency energy through the cathode electrode, the stability and uniformity of the plasma can be improved, and wherein by introducing the high frequency energy into the discharge space from a direction which is differentiated by more than 10° from the direction of the strong electric field of the microwave, it is possible to more diminish disturbance of the plasma by the cathode electrode. And optimizing the number, shape, size, etc. of the cathode electrode, the stability and uniformity of the plasma state can be more improved.

[0038]

Furthermore, in the present invention, by setting the ratio of the microwave energy/the high frequency energy and the power conditions thereof respectively in a prescribed range, the overlapping effect of the high frequency is more improved. And by applying a bias voltage, it is possible to relax a stress in the

deposited film and diminish defects thereof. This situation makes it possible to form a deposited film having excellent characteristics. Separately, in the present invention, when a cylindrical substrate is used as the substrate and the cylindrical substrate is rotated at such a rotating speed that the thickness of a deposited film formed on the cylindrical substrate becomes to be less than 2000 Å per one revolution, it is possible to form a deposited film uniformly over the entire surface of the cylindrical substrate. This situation makes it possible to form a deposited film having excellent characteristics at good reproducibility.

Table 1

high frequency	microwave
10MHz	2.45GHz
15 MHz	2.45GHz
20MHz	2.45GHz
30MHz	2.45GHz
51MHz	2.45GHz
105MHz	2.45GHz
150MHz	2.45GHz
200MHz	2.45GHz
250MHz	2.45GHz
300MHz	2.45GHz
350MHz	2.45GHz
450MHz	2.45GHz
600MHz	2.45GHz
1000MHz	2.45GHz

Table 2

SiH_4 gas flow rate (sccm)	150
He gas flow rate (sccm)	3000
inner pressure (mTorr)	10
microwave / high frequency	0.01～3.0

Table 3

high frequency	microwave / high frequency (power ratio)								
	0	0.01	0.05	0.1	0.3	0.5	1.0	1.5	2.0
10MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
15 MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
20MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
30MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
51MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
105MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
150MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
200MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
250MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
300MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
350MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
450MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
600MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0
1000MHz	1.0	1.01	1.05	1.1	1.5	1.8	2.0	2.0	2.0

Table 4

layer constitution / film-forming conditions	photoconductive layer	surface layer
row material gas & its flow rate		
SiH_4	280sccm	60sccm
He	2000sccm	2000sccm
CH_4	0sccm	450sccm
H_2	0sccm	100sccm
B_2H_6	5.0ppm	0ppm
inner pressure	20mtorr	15mtorr
high frequency power	900W	900W
microwave power	720W	720W
layer thickness	25 μ m	0.5 μ m

Table 5

interval between the two introduction times(sec) / frequency	0	0.1	0.5	1.0	5.0	10	30	60	120	300	600	900
10MHz	×	×	×	△	△	△	△	△	×	×	×	×
15MHz	×	×	×	○	○	○	○	○	△	×	×	×
20MHz	×	△	△	○	○	○	○	○	○	○	△	×
30MHz	×	△	○	○	○	○	○	○	○	○	△	×
51MHz	△	○	○	○	○	○	○	○	○	○	○	△
105MHz	△	○	○	○	○	○	○	○	○	○	○	△
150MHz	△	○	○	○	○	○	○	○	○	○	○	△
200MHz	△	○	○	○	○	○	○	○	○	○	○	△
250MHz	△	○	○	○	○	○	○	○	○	○	○	△
300MHz	×	△	○	○	○	○	○	○	○	○	△	×
350MHz	×	△	○	○	○	○	○	○	○	○	△	×
450MHz	×	△	○	○	○	○	○	○	○	△	△	×
600MHz	×	△	△	○	△	△	△	△	△	×	×	×
1000MHz	×	×	×	△	△	△	△	△	×	×	×	×

Table 6

inerval between the two introduction times(sec) / frequency	0	0.01	0.05	0.1	0.5	1.0	10	30	60	120	300	600
10MHz	×	×	×	△	△	△	△	△	×	×	×	×
15MHz	△	×	×	○	○	○	○	○	△	×	×	×
20MHz	△	△	△	○	○	○	○	○	○	○	△	×
30MHz	△	△	○	○	○	○	○	○	○	○	△	×
51MHz	△	○	○	○	○	○	○	○	○	○	○	△
105MHz	△	○	○	○	○	○	○	○	○	○	○	△
150MHz	△	○	○	○	○	○	○	○	○	○	○	△
200MHz	△	○	○	○	○	○	○	○	○	○	○	△
250MHz	△	○	○	○	○	○	○	○	○	○	○	△
300MHz	△	△	○	○	○	○	○	○	○	○	△	×
350MHz	△	△	○	○	○	○	○	○	○	○	△	×
450MHz	△	△	○	○	○	○	○	○	○	△	△	×
600MHz	△	△	△	○	○	○	○	○	△	△	×	×
1000MHz	×	×	×	△	△	△	△	△	×	×	×	×

Table 7

interval between the two introduction times(sec) / frequency	0	0.01	0.05	0.1	0.5	1.0	10	30	60	120	180	300
10MHz	△	△	△	△	△	△	△	△	×	×	×	×
15 MHz	△	△	○	○	○	○	○	○	△	×	×	×
20MHz	△	○	○	○	○	○	○	○	○	○	△	×
30MHz	△	○	○	○	○	○	○	○	○	○	△	×
51MHz	○	○	○	○	○	○	○	○	○	○	○	△
105MHz	○	○	○	○	○	○	○	○	○	○	○	△
150MHz	○	○	○	○	○	○	○	○	○	○	○	△
200MHz	○	○	○	○	○	○	○	○	○	○	○	△
250MHz	○	○	○	○	○	○	○	○	○	○	○	△
300MHz	△	○	○	○	○	○	○	○	○	○	△	×
350MHz	△	○	○	○	○	○	○	○	○	○	△	×
450MHz	△	○	○	○	○	○	○	○	○	△	△	×
600MHz	△	○	○	○	○	○	○	○	△	△	×	×
1000MHz	△	△	△	△	△	△	△	△	×	×	×	×

Table 8 (evaluation of ghost appearance)

ratio of microwave / high frequency / high frequency power	0	0.01	0.05	0.1	0.5	1.0	1.2	1.5	1.8	2.0	2.5	3.0
10	×	△	△	△	△	△	△	△	△	○	○	△
30	△	△	△	△	○	○	○	○	○	○	○	△
50	△	○	○	○	○	○	○	○	○	○	○	△
80	△	○	○	○	○	○	○	○	○	○	○	×
100	△	○	○	○	○	○	○	○	○	○	○	×
110	△	○	○	○	○	○	○	○	○	○	△	×
120	△	○	○	○	○	○	○	○	○	○	△	×
130	△	○	○	○	○	○	○	○	○	△	×	×
150	△	○	○	○	○	○	○	○	△	△	×	×
180	×	×	△	△	△	×	×	×	×	×	×	×
200	×	×	×	×	×	×	×	×	×	×	×	×

Note: high frequency power is a relative value(%) when the power with which the deposition rate is saturated under the conditions shown in Table 4 is set at 100%.

Table 9 (evaluation of blank exposure memory)

ratio of microwave / high frequency high frequency power	0	0.01	0.05	0.1	0.5	1.0	1.2	1.5	1.8	2.0	2.5	3.0
10	×	△	△	△	△	△	△	△	△	○	○	△
30	△	△	△	△	○	○	○	○	○	○	○	△
50	△	○	○	○	○	○	○	○	○	○	○	△
80	△	○	○	○	○	○	○	○	○	○	○	×
100	△	○	○	○	○	○	○	○	○	○	○	×
110	△	○	○	○	○	○	○	○	○	○	△	×
120	△	○	○	○	○	○	○	○	○	○	△	×
130	△	○	○	○	○	○	○	○	○	△	×	×
150	△	○	○	○	○	○	○	○	△	△	×	×
180	×	×	△	△	△	×	×	×	×	×	×	×
200	×	×	×	×	×	×	×	×	×	×	×	×

Note: high frequency power is a relative value(%) when the power with which the deposition rate is saturated under the condition shown in table 4 is set at 100%

Table 10(evaluation of charge retentivity unevenness)

ratio of microwave / high frequency high frequency power	0	0.01	0.05	0.1	0.5	1.0	1.2	1.5	1.8	2.0	2.5	3.0
10	×	△	△	△	△	△	△	△	△	○	○	△
30	△	△	△	△	○	○	○	○	○	○	○	△
50	△	○	○	○	○	○	○	○	○	○	○	△
80	△	○	○	○	○	○	○	○	○	○	○	×
100	△	○	○	○	○	○	○	○	○	○	○	×
110	△	○	○	○	○	○	○	○	○	○	△	×
120	△	○	○	○	○	○	○	○	○	○	△	×
130	△	○	○	○	○	○	○	○	○	○	△	×
150	△	○	○	○	○	○	○	○	○	△	×	×
180	×	×	△	△	△	×	×	×	×	×	×	×
200	×	×	×	×	×	×	×	×	×	×	×	×

Note: high frequency power is a relative value(%) when the power with which the deposition rate is saturated under the condition shown in table 4 is set at 100%

Table 11(evaluation of photosensitivity unevenness)

ratio of microwave / high frequency high frequency power	0	0.01	0.05	0.1	0.5	1.0	1.2	1.5	1.8	2.0	2.5	3.0
10	×	△	△	△	△	△	△	△	△	○	○	△
30	△	△	△	△	○	○	○	○	○	○	○	△
50	△	○	○	○	○	○	○	○	○	○	○	△
80	△	○	○	○	○	○	○	○	○	○	○	×
100	△	○	○	○	○	○	○	○	○	○	○	×
110	△	○	○	○	○	○	○	○	○	○	△	×
120	△	○	○	○	○	○	○	○	○	○	△	×
130	△	○	○	○	○	○	○	○	○	○	△	×
150	△	○	○	○	○	○	○	○	○	△	×	×
180	×	×	△	△	△	×	×	×	×	×	×	×
200	×	×	×	×	×	×	×	×	×	×	×	×

Note: high frequency power is a relative value(%) when the power with which the deposition rate is saturated under the condition shown in table 4 is set at 100%

Table 12 (evaluation of smeared image appearance)

ratio of microwave / high frequency high frequency power	0	0.01	0.05	0.1	0.5	1.0	1.2	1.5	1.8	2.0	2.5	3.0
10	×	△	△	△	△	△	△	△	△	○	○	△
30	△	△	△	△	○	○	○	○	○	○	△	△
50	△	○	○	○	○	○	○	○	○	○	○	△
80	△	○	○	○	○	○	○	○	○	○	○	×
100	△	○	○	○	○	○	○	○	○	○	○	×
110	△	○	○	○	○	○	○	○	○	○	△	×
120	△	○	○	○	○	○	○	○	○	○	△	×
130	△	○	○	○	○	○	○	○	○	○	△	×
150	△	○	○	○	○	○	○	○	○	○	△	×
180	×	×	△	△	△	×	×	×	×	×	×	×
200	×	×	×	×	×	×	×	×	×	×	×	×

Note: high frequency power is a relative value(%) when the power with which the deposition rate is saturated under the condition shown in table 4 is set at 100%

Table 13 (evaluation of white dot appearance)

ratio of microwave / high frequency high frequency power	0	0.01	0.05	0.1	0.5	1.0	1.2	1.5	1.8	2.0	2.5	3.0
10	×	△	△	△	△	△	△	△	△	○	○	△
30	△	△	△	△	○	○	○	○	○	○	△	△
50	△	○	○	○	○	○	○	○	○	○	○	△
80	△	○	○	○	○	○	○	○	○	○	○	×
100	△	○	○	○	○	○	○	○	○	○	○	×
110	△	○	○	○	○	○	○	○	○	○	○	×
120	△	○	○	○	○	○	○	○	○	○	△	×
130	△	○	○	○	○	○	○	○	○	○	△	×
150	△	○	○	○	○	○	○	○	○	○	△	×
180	×	×	△	△	○	○	△	△	×	×	×	×
200	×	×	△	△	×	×	×	×	×	×	×	×

Note: high frequency power is a relative value(%) when the power with which the deposition rate is saturated under the condition shown in table 4 is set at 100%

Table 14 (evaluation of black dot appearance)

ratio of microwave / high frequency high frequency power	0	0.01	0.05	0.1	0.5	1.0	1.2	1.5	1.8	2.0	2.5	3.0
10	×	△	△	△	△	△	△	△	△	○	○	△
30	△	△	△	△	○	○	○	○	○	○	△	△
50	△	○	○	○	○	○	○	○	○	○	○	△
80	△	○	○	○	○	○	○	○	○	○	○	×
100	△	○	○	○	○	○	○	○	○	○	○	×
110	△	○	○	○	○	○	○	○	○	○	○	×
120	△	○	○	○	○	○	○	○	○	○	△	×
130	△	○	○	○	○	○	○	○	○	○	△	×
150	△	○	○	○	○	○	○	○	○	△	△	×
180	×	×	△	△	○	○	△	△	×	×	×	×
200	×	×	×	△	△	×	×	×	×	×	×	×

Note: high frequency power is a relative value(%) when the power with which the deposition rate is saturated under the condition shown in table 4 is set at 100%

Table 15

layer constitution / film-forming conditions	charge injection inhibitation layer	photoconductive layer	surface layer
row material gas & its flow rate			
SiH_4	350sccm	350sccm	50sccm
H_2	2000sccm	2000sccm	2000sccm
C_2H_2	10sccm	0sccm	250sccm
NO	20sccm	0sccm	0sccm
B_2H_6	1000ppm	1.5ppm	0ppm
inner pressure	25mtorr	25mtorr	20mtorr
power ratio of microwave/ high frequency	0.8	0.8	0.8
layer thickness	3 μ m	25 μ m	0.5 μ m

Table 16

evaluation item	Example 1	Comparative example 1	Comparative example 2	Comparative example 3	Comparative example 4	Comparative example 5
ghost appearance	○	×	×	×	△	△
blank exposure memory	○	×	×	×	△	△
charge retentivity unevenness	○	△	×	×	△	×
photosensitivity unevenness	○	△	×	×	△	×
smeared image appearance	○	△	△	×	△	△
white dot appearance	○	△	○	×	△	△
black dot appearance	○	△	△	×	△	△

Table 17

layer constitution / film-forming conditions	charge injection inhibitation layer	charge transportation layer	charge generation layer	surface layer
row material gas & its flow rate				
SiH_4	350sccm	350sccm	350sccm	50sccm
H_2	2000sccm	2500sccm	2000sccm	2000sccm
C_2H_2	50sccm	30sccm	0sccm	450sccm
NO	20sccm	0sccm	0sccm	0sccm
B_2H_6	1000ppm	10ppm	1.5ppm	0ppm
inner pressure	15mtorr	15mtorr	15mtorr	10mtorr
power ratio of microwave/ high frequency	0.8	0.8	0.8	0.8
layer thickness	3 μ m	20 μ m	3 μ m	0.5 μ m

Table 18

evaluation item	Example 2	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10
ghost appearance	○	×	×	×	△	△
blank exposure memory	○	×	×	×	△	△
charge retentivity unevenness	○	△	×	×	△	△
photosensitivity unevenness	○	△	×	×	△	×
smeared image appearance	○	△	△	△	△	△
white dot appearance	○	△	○	×	△	△
black dot appearance	○	△	△	×	△	△

Table 19

layer constitution / film-forming conditions	photoconductive region 1	photoconductive region 2	surface layer
row material gas & its flow rate			
SiH_4	400→250sccm	250sccm	250→50sccm
He	1000→800sccm	800sccm	800→200sccm
CH_4	250→0sccm	0sccm	0→450sccm
SiF_4	0sccm	0sccm	0→20sccm
B_2H_6	50→1.5ppm	1.5ppm	0ppm
H_2	800→0sccm	0sccm	100sccm
inner pressure	15mtorr	12mtorr	12mtorr
power ratio of microwave/ high frequency	0.8	0.8	0.8
layer thickness	25 μ m	3 μ m	0.5 μ m

Table 20

evaluation item	Example 2	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10
ghost appearance	○	×	×	×	△	△
blank exposure memory	○	×	×	×	△	△
charge retentivity unevenness	○	△	×	×	△	△
photosensitivity unevenness	○	△	△	△	△	△
smeared image appearance	○	△	△	△	△	△
white dot appearance	○	△	○	×	△	△
black dot appearance	○	△	△	×	△	△

【Brief Description of the Drawings】

FIGs. 1, 4, 5 and 6 are schematic cross-sectional views respectively illustrating the layer constitution of an example of an electrophotographic light receiving member which is formed by the deposited film-forming apparatus and the deposited film-forming method of the present invention.

FIG. 2(A) is a schematic longitudinal section view illustrating an example of a deposited film-forming apparatus by a plasma CVD process for forming a deposited film on a cylindrical substrate in the present invention. FIG. 2(B) is a schematic cross-sectional view taken along the line X-X in FIG. 2(A).

FIG. 3(A) is a schematic longitudinal section view illustrating an example of a deposited film-forming apparatus by a plasma CVD process of overlapping a microwave for forming a deposited film on a cylindrical substrate in the present invention. FIG. 3(B) is a schematic cross-sectional view taken along the line X-X in FIG. 3(A).

【Explanation of reference numerals】

100, 400, 500, 600 --- electrophotographic light receiving member

101, 401, 501, 601 --- substrate

102, 402 --- photoconductive layer

103, 403, 503, 603 --- surface layer

404, 504 --- charge injection inhibition layer

505 --- charge transportation layer

506 --- charge generation layer

607 --- photoconductive region 1

608 --- photoconductive region 2

201, 301 --- reaction vessel

202 --- cathode electrode

302 --- gas introduction pipe serving also as cathode electrode

203, 303 --- matching box

204, 304 --- high frequency power source

205, 305 --- substrate

206, 306 --- substrate holder

207, 307 --- substrate heater

208, 308 --- exhaust pipe

209, 309 --- rotary shaft

210, 310 --- motor

211, 311 --- gas introduction pipe

212, 312 --- discharge space

213, 313 --- waveguide

214, 314 --- microwave introducing dielectric window

215, 315 --- direct current power source (bias power source)

FIG.1

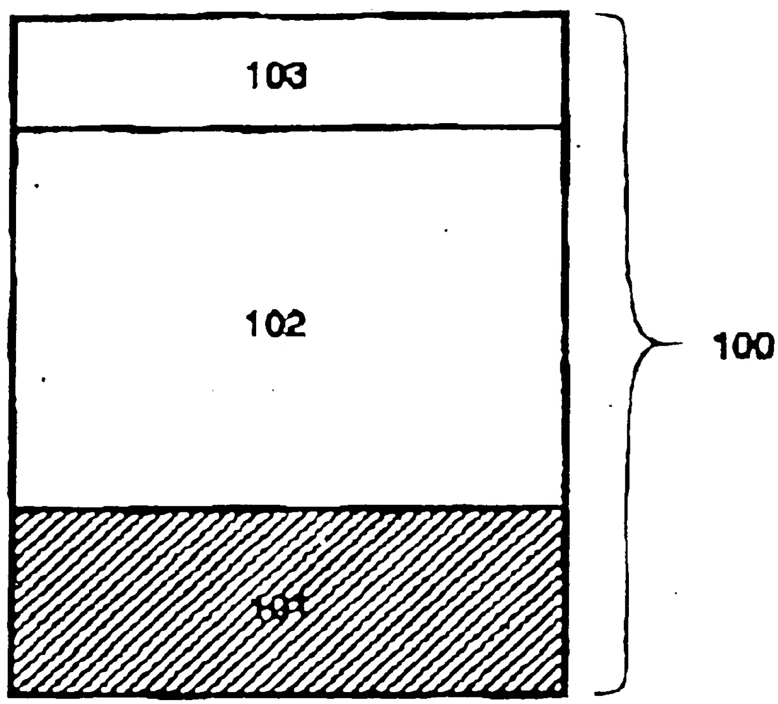

FIG.2

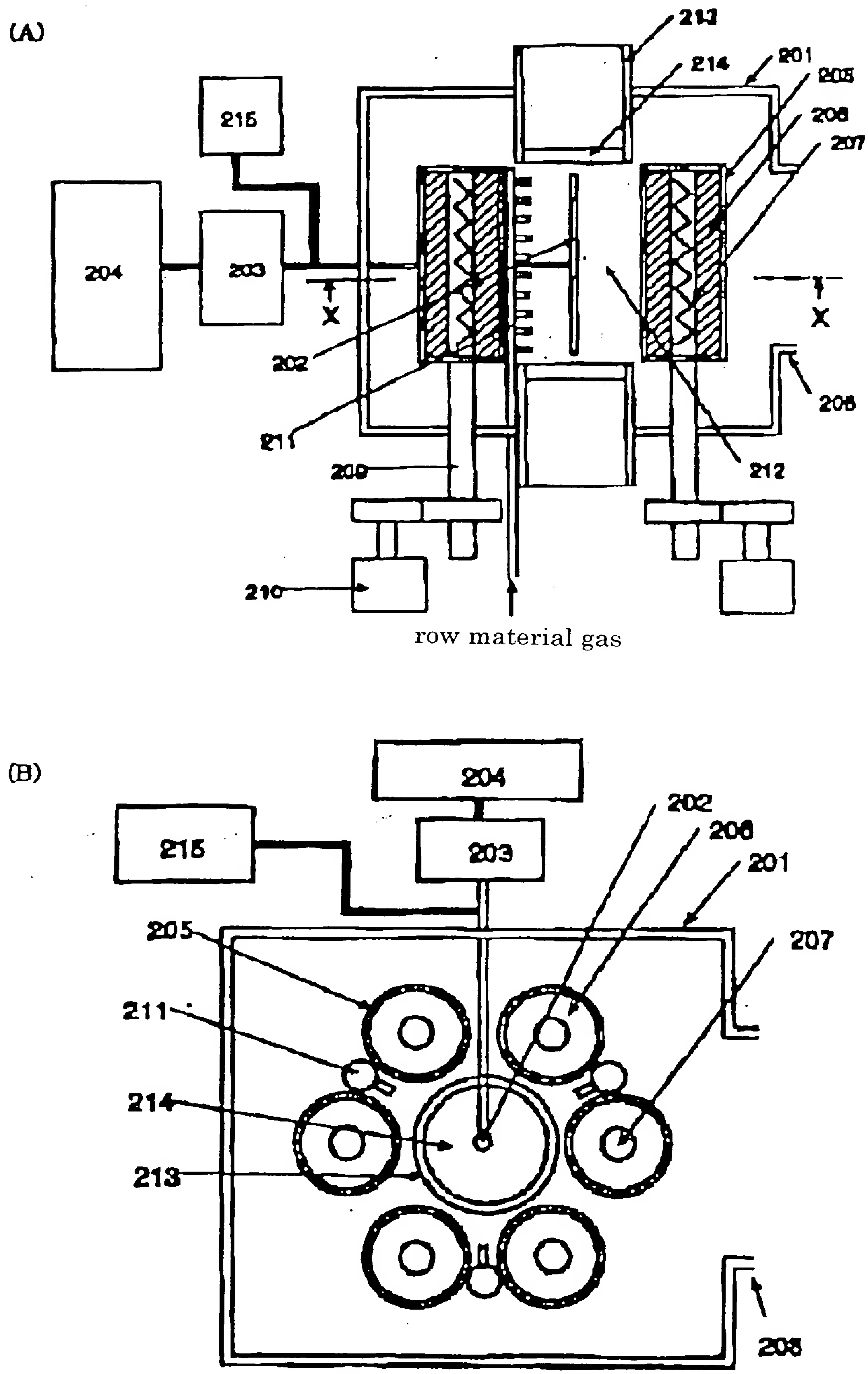
(A)
213
214
201
205
206
207
215
204
203
X
X
202
211
208
209
212
210
row material gas
(B)
204
215
203
202
206
201
205
207
211
214
213
208

FIG.3

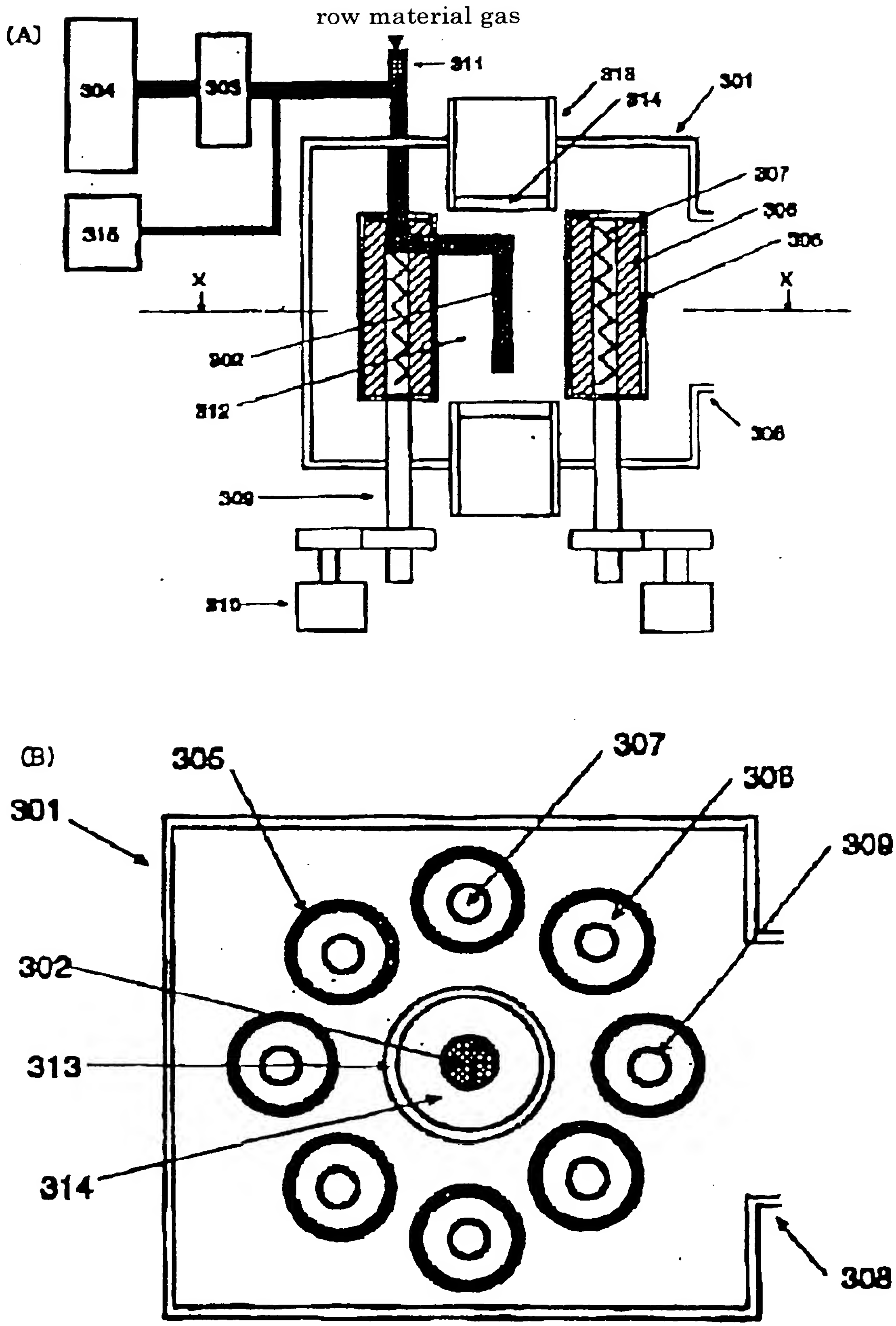
(A)
row material gas
304
303
315
311
301
307
302
312
309
310
X
X
(B)
305
307
301
302
313
314
308

FIG.4

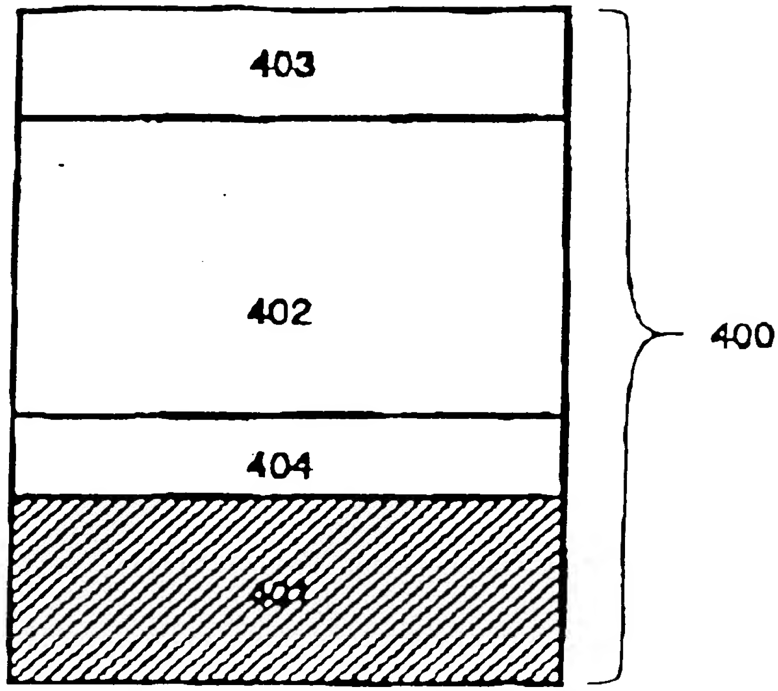

FIG.5

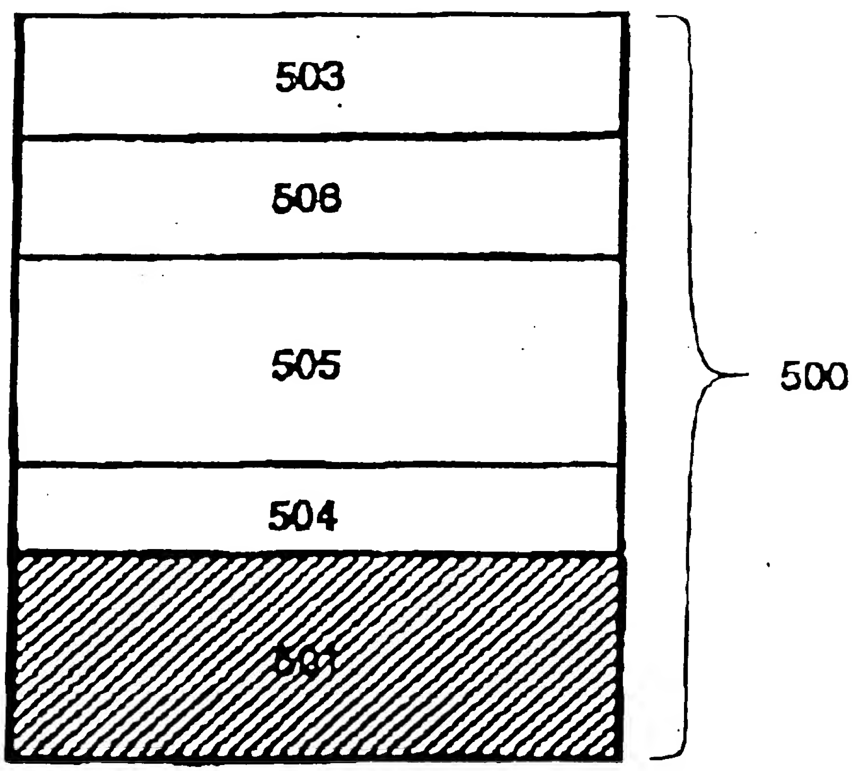

FIG.6